

i.e., **c** is the direction of easy magnetization, then the following statements hold:

- (1) The octahedral ferric ions lie in rows parallel to **a**.
- (2) The octahedral ferrous ions lie in rows parallel to **b**.
- (3) The magnetic moments of all ions are parallel or antiparallel to **c**.
- (4) The **a** axis is longer than the **b** axis.

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Effect of Degree of Orientation and Crystal Size on the Scattering of 20-kev Electrons by Aluminum*

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The energy distribution of 20-kev electrons scattered by aluminum has been measured as a function of degree of crystalline orientation and foil thickness. For equal physical thickness the foils with higher degree of orientation are electron-optically thinner. Over a range of thickness from 35 to 500 Å, the values of the first two characteristic losses are 6.3 ± 0.1 eV and 15.0 ± 0.1 eV. They exhibit no systematic change with thickness greater than the experimental uncertainty. The intensity ratio between the two losses is essentially constant within this range. It is concluded that the low-lying (6.3 eV) loss is not due to the depolarization effect of grain boundaries.

IN an earlier publication¹ it was noted that the distribution of electrons scattered by gold was strongly influenced by the degree of crystalline orientation, but the instrumental resolution was insufficient to show detail. When a new analyzer became available that had an energy resolution of less than 1 eV and an angular resolution less than 1 milliradian, it became possible to obtain quantitative data.

Foils of cp aluminum were prepared by vacuum evaporation at a residual gas pressure of less than 10^{-4} mm Hg on a freshly cleaved rocksalt substrate. In the case of the polycrystalline samples this was at room temperature, and in the single-crystal samples at the known epitaxy temperature of 440°C. A few partially oriented samples were prepared with substrates at intermediate temperatures obtained by use of a gradient furnace.² The evaporation rate was uncontrolled but rapid, so that the process was completed in less than 1 minute. The rocksalt was masked to give four $\frac{1}{8}$ -in. disks. The four disks were floated off the rocksalt onto a water surface and then three were picked up, one over a 0.014-in. hole in the scattering mount, another on a standard 200-mesh diffraction camera mount and the

third on a microscope slide for thickness measurements in a Tolansky³ interferometer.

Figures 1 and 2 show typical diffraction patterns of "unoriented" and "oriented" films prepared in this way. Figure 3 presents a typical energy distribution at zero scattering angle for a polycrystalline sample. The char-

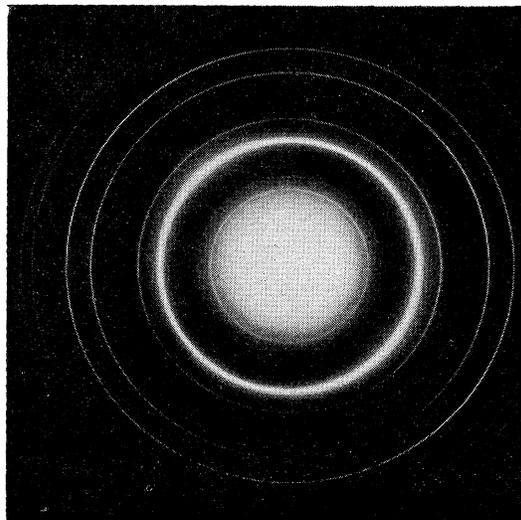


FIG. 1. The electron diffraction pattern of a typical unoriented sample of thickness 900 Å.

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¹ Marton, Simpson, and McCraw, *Phys. Rev.* **99**, 495 (1955).

² L. Marton and J. A. Suddeth, *Rev. Sci. Instr.* **29**, 440 (1958).

³ S. Tolansky, *Multiple Beam Interferometry* (Oxford University Press, New York, 1948).

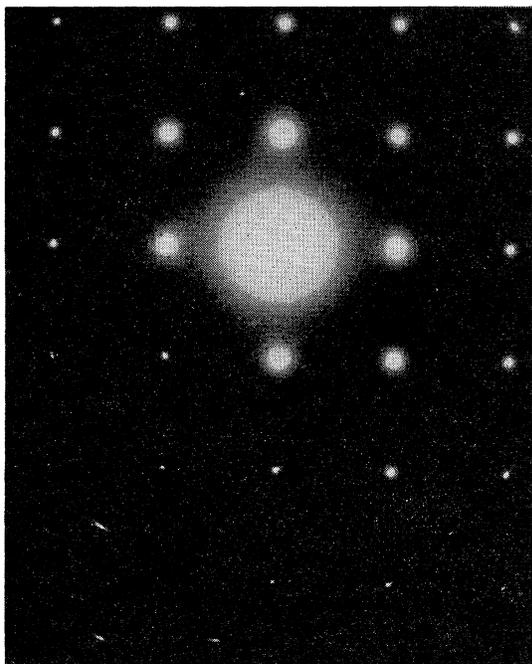


FIG. 2. The electron diffraction pattern of a typical oriented sample of thickness 1400 Å. Note the almost perfect single-crystal pattern.

acteristic energy loss⁴ at ~ 15 eV and its multiples are prominent features. The intensities on the recording are on a quasi-logarithmic scale which was converted to actual intensities by a calibration against a detector of known linearity. To avoid the errors involved in absolute intensity measurements and to compensate for the absorption of the different foil thicknesses, the data are presented as a series of ratios.

Figure 4 is a plot of the ratio of elastically scattered electrons to electrons of the characteristic loss value at

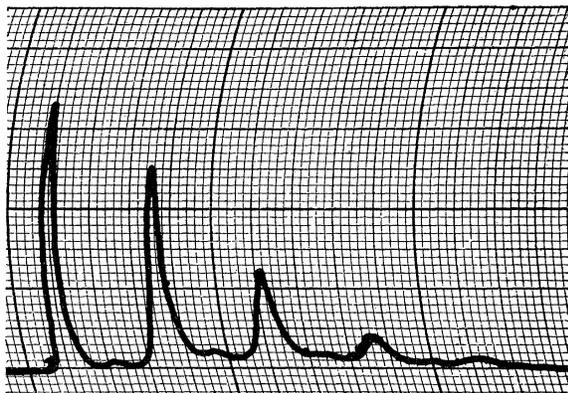


FIG. 3. The energy spectrum of electrons scattered by the unoriented aluminum sample. Note the characteristic 15-volt loss and its multiples. The intensity scale is logarithmic.

⁴ Marton, Leder, and Mendlowitz, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. VII, p. 183.

two scattering angles, $\theta=0$ and $\theta\sim 6\times 10^{-2}$ radian [the (220) diffraction maximum], for unoriented and oriented foils. The partially oriented foils gave points scattered between the two plotted curves. The desired diffraction maximum was found by initial calculation from the constants of the instrument and the nominal 20-keV acceleration voltage. The final adjustment was made by adjusting θ for the local maximum of elastically scattered electrons. In the case of the single crystals a further adjustment of the specimen orientation about the beam axis ϕ was made using the same criteria. Both adjustments were simplified by the fact that, in the region of the diffraction maximum, the intensity of the characteristic loss exceeds the intensity of the elastically scattered electrons except at the diffraction maximum itself.

The bars on one of the curves (Fig. 4) represent the spread in values obtained from two measurements on each of three samples of the same evaporation. All the

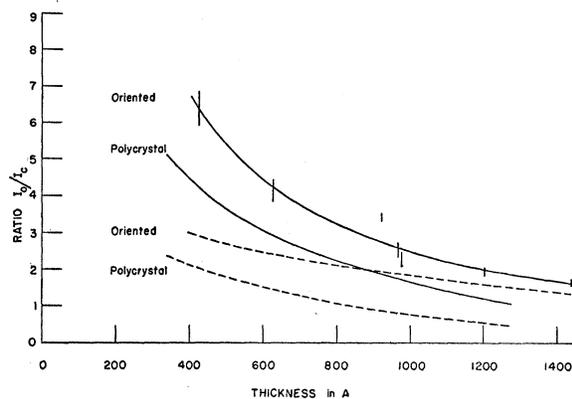


FIG. 4. The ratio of the characteristic loss to the elastic transmission as a function of thickness and degree of orientation. The solid lines are at zero angle, the dotted at the (220) diffraction maximum.

errors are reported as errors in intensity ratio although some arise from thickness differences between the supposedly identical samples. Multiple interferometry measurements show that this error may be as high as 50 Å.

There are two features that are immediately obvious. First, the energy distribution at the diffraction maximum is significantly different from the one at zero angle. Moreover, this difference depends on both the sample thickness and the degree of crystalline order. This behavior is of considerable importance in precision diffraction, since the "center of gravity" of the diffraction ring moves to larger angles in polycrystalline samples and as the thickness increases. This effect has been reported⁵ but has been ascribed to a change in lattice spacing. It appears necessary to repeat the diffraction experiments with apparatus capable of analyzing the energy spectra in the maxima, since our

⁵ Y. Fukano, *J. Phys. Soc. Japan* **10**, 420 (1955).

results show a mean energy shift of the correct magnitude and direction to explain the observed shift of the maxima. Further support for this point of view is given by some preliminary work with an energy filter lens where the shift was not observed.⁶ The same effect on the broad and intense 20-ev loss of Au may offer an explanation of the difficulties experienced by Rymer in his attempts to verify the de Broglie relationship by comparing electron and x-ray lattice spacings of this material.⁷

Second, the more nearly single-crystal samples for equal thickness scatter less or are electron-optically thinner.

This observation is consistent with their visual transparency and with the optical data of Sennett and Scott⁸ showing that for metals the transmission increases sharply as order increases. Similarly, more marked effects in germanium were noted by Gebbie.⁹

To extend the measurements to still smaller crystal-lite sizes, use was made of the linear relationship between grain size and foil thickness reported by Kuwabara.¹⁰ For these experiments the aluminum was evaporated onto carbon-coated collodion substrates. To prevent migration or grain growth the aluminum was immediately covered with approximately 50 Å of carbon. The carbon was applied without exposing the foils to air by the method developed by Bradley.¹¹ The variation in thickness was achieved by placing the supports a varying distance from the evaporation source. The absolute thickness was then computed by inverse square relationship from the thickest foil which was measured interferometrically. Five samples varying in thickness from 35 Å to 500 Å were prepared with the substrate at room temperature and another five at liquid nitrogen temperature.

The energy spectra of these foils were measured at the highest obtainable resolution (0.1 ev) and with the energy scale compared with a standard cell.

An earlier measurement, made by one of us (HW) on similar samples with an entirely different analyzer, had given some indication of a slight (~ 0.4 ev) systematic increase of the characteristic loss with decreasing grain size. This shift was in the opposite sense and much smaller than that reported by Friedmann¹² for selenium over the same range of thickness.

Our present measurements show no systematic shift within the thickness range studied with the maximum deviation in the ten measurements less than 0.3 ev.

The same measurements were used to investigate the applicability of the theory of Ritchie¹³ as to the origin

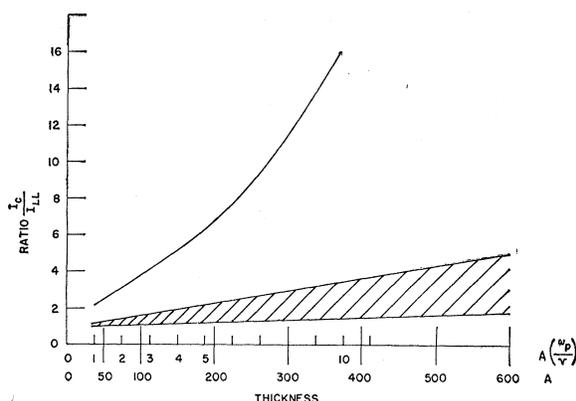


Fig. 5. The intensity ratio between the characteristic loss and the low-lying loss as a function of thickness. The shaded region covers experimental points; the solid line is the predicted dependence. ω_p is the plasma frequency and v the initial electron velocity; thickness $\times (v/\omega_p) = t$ (the top scale of the abscissa).

of the low-lying energy loss. He suggests that this loss is a "lowered" plasma loss. The lowering is caused by a depolarization effect because of the boundaries of the finite grains. Such a loss would appear at a value below the plasma loss by a factor of $1/\sqrt{2}$ if only the thickness were finite or $1/\sqrt{3}$ if the grains are assumed to be spherical.

The average value of the characteristic (plasma) loss was found to be 15.0 ± 0.1 ev and for the low-lying loss 6.3 ± 0.1 ev. The measured ratio is then 0.42 ± 0.1 .

The same theory predicts that as the grain size is reduced, the intensity ratio between the characteristic and low-lying loss should decrease in a particular manner.

In all, thirty specimens were measured, the ten mentioned above and twenty additional ones ranging in thickness between 350 and 500 Å whose thicknesses were directly measured and which were self-supporting. The results are shown in Fig. 5. All the points lie within the shaded area of the graph. For comparison, the expected variation taken from Fig. 1 of Ritchie is shown by the solid line. The calculation of Ritchie is for the total cross section while the measurements are of the cross section within a small acceptance angle ($\sim 10^{-3}$ radian) about the forward direction. The justification of the direct comparison lies in the experimental fact that essentially all the scattered beam lies within this narrow cone. We believe the cause of this peaking in the forward direction is diffraction. Even in polycrystalline samples a high degree of order exists and the diffraction maxima, especially the zero order, are very prominent. Measurements taken on 200 Å thick polycrystalline aluminum show that the intensity, within a 10^{-3} -radian cone at an angle of 5×10^{-3} radian, is only one hundred thousandth (10^{-5}) of the intensity within the same cone in the forward direction. The initial falloff has an angular dependence of the order of θ^{-5} to θ^{-8} . The plasma theory predicts an angular dependence

⁶ H. Boersch (private communication).

⁷ T. B. Rymer and K. H. R. Wright, Proc. Roy. Soc. (London) **A215**, 550 (1952).

⁸ R. S. Sennett and G. D. Scott, J. Opt. Soc. Am. **40**, 203 (1950).

⁹ O. S. Heavens, *Optical Properties of Thin Solid Films* (Butterworths Publications, London, 1955), p. 170.

¹⁰ S. Kuwabara, J. Phys. Soc. Japan **12**, 637 (1957).

¹¹ D. E. Bradley, Brit. J. Appl. Phys. **5**, 65 (1954).

¹² H. Friedmann, Z. Naturforsch. **11**, 373 (1956).

¹³ R. H. Ritchie, Phys. Rev. **106**, 874 (1957).

of the electron losses considerably less peaked (θ^{-2}). Ferrell¹⁴ assumed that the difference between the observed distribution of the characteristic losses and that calculated from the plasma theory is due to "contamination" of the characteristic loss by the no-loss peak. Evidence obtained previously by us¹⁵ does not seem to bear out this assumption. Ritchie¹⁶ has calculated I_c/I_{LL} versus foil thickness assuming the angular distribution given by plasma theory and a detector with an acceptance of 1 milliradian. He finds considerably better agreement with the experiment than shown here. Although our explanation of the peaking as a diffraction phenomenon may be incorrect we feel that the peaking itself is a well-established experimental fact. The most exact comparison with the theory would

¹⁴ R. A. Ferrell, Phys. Rev. **101**, 554 (1956).

¹⁵ Simpson, McCraw, and Marton, Phys. Rev. **104**, 64 (1956).

¹⁶ R. H. Ritchie (private communication).

be somewhere between the extremes represented by the differential and integral cross section. We feel that the experimental facts support our choice of the integral cross section for comparison. The shaded area is a measurement of the internal consistency of our data and is not intended to imply an accuracy. Known sources of possible error in thickness and measured intensity could give uncertainties of 50% in the region below 200 Å.

Since neither the predicted value of low-lying loss nor its dependence on grain size is confirmed, it must be concluded that the 6.3-eV loss of aluminum is not a "lowered" plasma loss.

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Elastic and Piezoelectric Constants of Alpha-Quartz

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The elastic and piezoelectric constants of alpha-quartz have been determined by the resonance (previously known as dynamic) method employing the extensional mode of bars and the contour-extensional mode I (Lamé mode) of square plates. It is believed that this approach results in very accurate values.

THE elastic and piezoelectric constants of alpha-quartz have been determined by several methods, e.g., the static method,¹ the resonance (previously known as dynamic) method,²⁻⁵ the ultrasonic method,⁶ and by means of light diffraction.⁷

By employing the resonance method, the elastic and piezoelectric constants are derived from measured values of the series resonance frequency, the motional capacitance, and the dimensions of appropriately cut and excited specimens. The constants to be determined and the quantities measured are related by the mathematical solution for the frequency and the displacement of the mode of motion for the specimens considered. Extensional modes of narrow bars and contour modes of square plates are determined by the elastic compliances s_{pq} and the piezoelectric strain

constants d_{jp} . The thickness modes of thin plates lead to the elastic stiffnesses c_{pq} and the piezoelectric stress constants e_{jp} . If one set of constants, for example s_{pq} and d_{jp} , is known, the corresponding c_{pq} and e_{jp} can be calculated.

The resonance method is considered as a simple and very reliable means for determination of the elastic and piezoelectric constants as the measurements can be performed with a high degree of accuracy provided sufficiently large crystals are available. Furthermore, the conversion of these measurements into the material constants is accomplished by means of a rigorous mathematical solution when the extensional mode of bars and contour-extensional mode I (Lamé mode) of square plates are used. For other modes, close approximations are known. The resonance method is described in detail by Bechmann and Ayers⁸ and has been adopted as an Institute of Radio Engineers standard.⁹

The results should be independent of the modes of motion used. Measurements have shown that the values

¹ W. Voigt, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1928).

² J. V. Atanasoff and P. J. Hart, Phys. Rev. **59**, 85 (1941).

³ A. W. Lawson, Phys. Rev. **59**, 838 (1941).

⁴ W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

⁵ R. Bechmann, Proc. Phys. Soc. (London) **B64**, 323 (1951).

⁶ S. Bhagavantam, Proc. Indian Sci. Congr., 33rd Congr. Part II, (1946).

⁷ O. Nomoto, Proc. Phys.-Math. Soc. Japan **25**, 240 (1943).

⁸ R. Bechmann and S. Ayers, *Piezoelectricity* (Her Majesty's Stationery Office, London, 1957), Rept. No. 4, Selected Engineering Reports, Post Office Research Station.

⁹ Inst. Radio Engrs., Proc. Inst. Radio Engrs. **46**, 764 (1958).

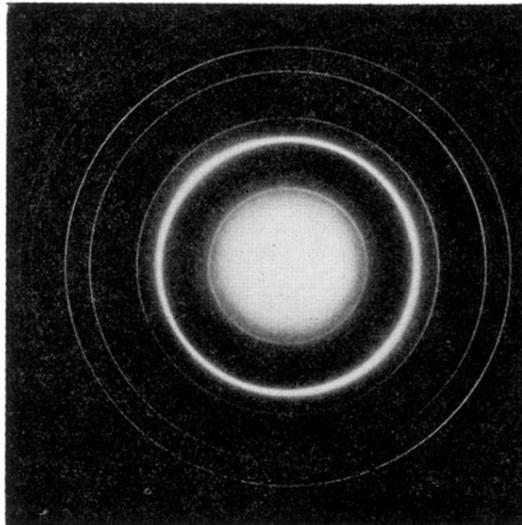


FIG. 1. The electron diffraction pattern of a typical unoriented sample of thickness 900 Å.

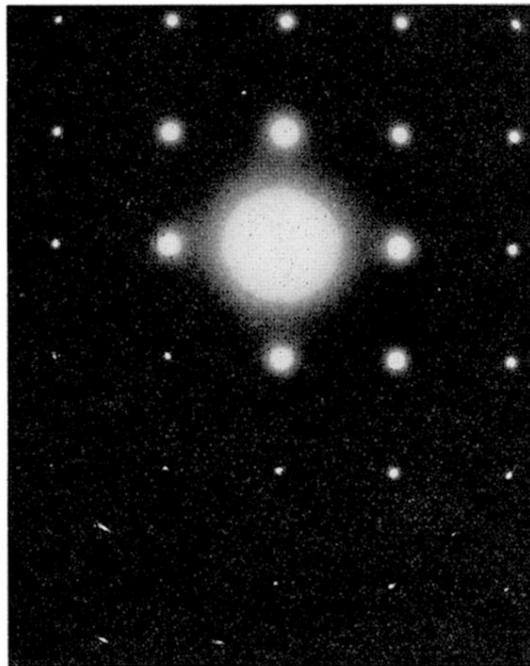


FIG. 2. The electron diffraction pattern of a typical oriented sample of thickness 1400 Å. Note the almost perfect single-crystal pattern.